Charge distribution in cyclopentadienylcycloheptatrienylmetal and related compounds

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SUMMARY

In this thesis some investigations concerning the charge distribution in sandwich compounds with two different rings are described. These investigations mainly deal with the compounds $(C_5H_5)M(C_7H_7)$ with M=Ti, V and Cr. In a number of cases the corresponding 4d transition metal compounds (M= Zr, Nb and Mo) have also been investigated. Some work has also been done on the compounds $(C_5H_5)Ti(C_8H_8)$ and $(C_5H_5)Ti(C_9H_9)$.

In chapter 1 some relevant results of investigations on symmetric sandwich compounds such as the dicyclopentadienyl and the dibenzenemetal compounds are summarized. With the aid of MO theory and the results of investigations on symmetric sandwich compounds, some predictions are made about the charge distribution in the "mixed" sandwich compounds mentioned above.

The results of metallation reactions of the $(C_5H_5)M(C_7H_7)$ compounds with M=Ti, V and Cr are described in chapter 2. The most remarkable result of these reactions is that substitution of the Ti compound occurs very easily and predominantly in the C_7H_7 ring. Substitution of the V (and Cr) compound, on the contrary, is more difficult and mainly takes place in the C_5H_5 ring.

Chapter 3 deals with ^{13}C NMR measurements on the diamagnetic series of the 3- and 4d transition metal compounds. These investigations indicate that in $(C_5H_5)Ti(C_7H_7)$ and in the corresponding Zr compound the highest negative charge is found on the carbon atoms of the C_7H_7 ring, whereas in the Cr compound the highest negative charge is on the C_5H_5 ring.

In chapter 4 photoelectron-spectroscopy measurements are discussed. This chapter consists of two parts, e.i. part 1 dealing with X-ray photoelectron spectroscopy (or ESCA) and part 2 dealing with UV photoelectron spectroscopy (or PES).

The ESCA measurements show that the positive charge of the metal atom in the compounds $(C_5H_5)M(C_7H_7)$ with M=Cr, V and

Ti increases in the sequence Cr<V<Ti. Furthermore, they show that in the Cr compound the C_5H_5 ring has a higher negative charge than the C_7H_7 ring; that in the V compound both rings carry about equal negative charges; and that in the Ti compound the highest negative charge resides on the C_7H_7 ring.

The results of the PES measurements show that the e_2 orbitals of the ligand become of more importance for the bonding with a transition metal as the ring size increases. This is in agreement with the MO considerations given in chapter 1.

In chapter 5 the results of metallation reactions and ESCA measurements on $(C_5H_5)Ti(C_8H_8)$ are described. This compound is much more difficult to metallate than $(C_5H_5)Ti(C_7H_7)$ and the substitution occurs predominantly in the C_5H_5 ring. This indicates that the C_5H_5 ring is more negatively charged than the C_8H_8 ring, which is in agreement with the results of the ESCA measurements. These findings can be explained in terms of MO considerations.

The synthesis and some properties of the compound $(C_5H_5)Ti(C_9H_9)$ are described in chapter 6. IR, NMR and mass spectra of the compound indicate the presence of a planar C_5H_5 ring, while the C_9H_9 ring is present as a heptahapto ligand.

The results of the investigations are summarized in chapter 7. The observed differences in charge distribution in the series $(C_5H_5)M(C_7H_7)$ with M=Ti, V and Cr and the rather unexpected charge distribution in $(C_5H_5)Ti(C_8H_8)$ are discussed in terms of qualitative MO considerations. Explanations for the short Ti-C distances in the $Ti(C_7H_7)$ moiety, the unsuccessful attempts to prepare compounds such as $(h^7\text{-}C_7H_7)_2Ti$ and $(h^5\text{-}C_5H_5)Ti(h^9\text{-}C_9H_9)$ and the lack of 18-electron sandwich compounds of Ti and V are also proposed.

In chapter 8 details of the experimental work related to the foregoing chapters are given.